THE PRACTICAL ADVANTAGES OF THE GOOCH CRUCIBLE IN THE DETERMINATION OF THE TOTAL AND VOLATILE SUSPENDED MATTER IN SEWAGE.

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THE determination of the total and volatile suspended matter in sewage and sewage effluents has recently become of considerable importance, owing to the rapidly increasing number of sewage disposal problems in which conditions necessitate the adoption of filters of coarse-grain material, generally preceded by settling or septic tanks. In determining the efficiency of these latter-day sewage works, and in special investigations incidental to the design of plants of this character, it is highly important that accurate data be obtained upon the amount and character of the suspended matter in the raw sewage. For it is this point which, in a very large measure, controls decisions regarding the character of the preparatory treatment which is best fitted to a given set of conditions, and to which are closely related, also, decisions regarding the character of the finishing process.

In the course of the investigations at the Testing Station, Columbus, Ohio, the question of the removal of the suspended matter in crude sewage under different velocities was made the subject of special study, as will be reported elsewhere, necessitating a large number of determinations of both total and volatile suspended matter. Owing to the pressure of other lines of routine analytical work, and the large amount of expensive apparatus necessary in connection with the usual indirect platinum evaporation method for work of this character, the direct Gooch crucible method, used to advantage by McGowan[1] in sewage work, was substituted in a material measure for the more tedious indirect platinum method. Our experience in this connection indicates that this direct method possesses advantages sufficiently distinct to warrant its serious consideration by other workers

[1] *Fourth Report Royal Com. on Sewage Disp.*, 4, 30, Pt. 5, p. 47.

interested in the determination of total and volatile suspended matter in sewage.

So far as we are able to learn, the application of the Gooch crucible to the determination of the suspended matter in water was first suggested by Thomas and Hall[1] of Philadelphia; in sewage analysis, so far as we are aware, it was developed by McGowan, as described in detail in the *Chemical Report to the Royal Commission on Sewage Disposal*, 1905. The author states, as a result of his experience, that the Gooch crucible may be relied upon to give very accurate data upon suspended matter in sewages, with a minimum expenditure of time. We have carefully studied, under Columbus conditions, the reliability and the general practical advantages of this method for the determination of suspended matter in sewage and sewage effluents, and our results indicate the correctness of the assertions of the English workers.

This paper will be devoted chiefly to a detailed account of our experience with the Gooch crucible in sewage work, referring to the determinations of the volatile, as well as to the total suspended, matter, together with a discussion of the relative merits, from a practical standpoint, of the Gooch crucible and the indirect platinum methods.

DETAILS OF THE COLUMBUS METHOD FOR THE DETERMINATION OF THE TOTAL AND VOLATILE SUSPENDED MATTER BY THE GOOCH CRUCIBLE.

Preparation of asbestos.—Asbestos adapted for use in the Gooch crucible may be readily prepared from the granular commercial product by digestion on a water bath in strong hydrochloric acid for several hours.[2] By successive decantations with distilled water, the acid is completely removed, leaving the asbestos practically free from iron. High-grade, long fiber asbestos has not been found to yield as good results as the commercial asbestos purified as above described.

Preparation of mat.—Prepare a dilute cream of the washed asbestos, which must be free from coarse particles, attach the crucible* to the filter flask in the usual manner, start the suction, and form a mat about $\frac{1}{16}$ inch thick upon the bottom of the crucible. After the asbestos has drained completely, apply to the crucible a small quantity of distilled water. If the mat is of the correct thickness, the distilled water will pass through the filter at the rate of about 50 drops per minute. Place the crucible in an oven at 110°–120° C. for 15 minutes; remove and ignite in a radiator for five minutes; cool in a desiccator and weigh. Before each weighing it is expedient to cleanse thoroughly with a soft cloth the outside surfaces of the crucibles. In the absence

[1] *Jour. Am. Chem. Soc.*, 1902, 24, p. 538.

[2] *Fourth Report Royal Com. on Sewage Disp.*, 4, Pt. 5, p. 47.

*Royal Berlin solid porcelain crucibles were used for this work.

of a platinum radiator, we have found that a four-inch nickel dish, heated to a dull red heat, admirably serves the purpose of this method. During the ignition it has been the practice to allow the crucible to rest directly upon the bottom of the radiator

Filtration.—Use 50 c.c., 100 c.c., or more of the sample, decanting into the crucible as great an amount as possible of the supernatant water before the main portion of the suspended matter is applied thereto; in this way the filtration will be the more rapidly accomplished. Allow the liquid to disappear completely before adding subsequent portions of the sample, also to facilitate filtration. When the filtration is completed, rinse out the flask with about 15 c.c. of distilled water. To guard against imperfect filtration, it is advisable to apply the suction gradually. In case the filtrates are cloudy, they must be refiltered until clear. With a properly prepared mat, our experience indicates that imperfect filtration is of rare occurrence.

Drying and igniting.—The crucible is dried at 110°–120° C. for one hour, cooled in a desiccator, and weighed, the increase in weight representing the *total suspended matter* in the sample. To obtain the *volatile suspended matter*, the weighed crucible is ignited in the radiator at a low red heat, for 10 minutes or to constant weight. The completeness of the ignition may be judged by the appearance of the residue. The suspended matter in sewage work is usually black in color, owing to the presence of sulphide of iron. On ignition, as is evident, this is oxidized to ferric oxide, which usually predominates sufficiently to impart to the thoroughly ignited residue, when cool, a reddish-brown color. Our experience indicates that an ignition of 10 minutes is sufficient to effect a complete oxidation of the organic matter present.

Removal of mat.—To prepare the crucibles for further use, remove the mat, rinse well in tap water, and finally with distilled water, making sure that the perforations in the bottom of the crucibles are not clogged.

A synopsis of the technique is as follows:

1. Prepare the asbestos mat, $\frac{1}{16}$ inch thick.
2. Wash in distilled water.
3. Dry the crucible at 110°–120° C. for 15 minutes.
4. Ignite for five minutes.
5. Weigh. (No. 1.)
6. Affix crucible to filter flask and start suction pump.
7. Filter sample, decanting supernatant into crucible.
8. Wash residue with distilled water.
9. Dry for one hour at 110°–120° C.
10. Cool in desiccator.
11. Weigh. (No. 2.)
12. Ignite at low red heat in a radiator for 10 minutes.
13. Cool in desiccator.
14. Weigh. (No. 3.)

Weight No. 1=weight of crucible and mat.
Weight No. 2=ditto, plus suspended matter.
Weight No. 3=same as No. 2, minus volatile matter.

RELATIVE RAPIDITY AND ACCURACY OF THE GOOCH CRUCIBLE METHOD.

The determination of the solid matters in sewage and in water, as is well known, requires considerable care and involves a large expen-

diture of time. Where suspended matter results alone are desired, the advantages of a direct method are at once apparent. With the Gooch method the results under routine operation should be available in at least two hours.

That an idea may be had of the accuracy of the Gooch method for the determination of suspended matter in samples wherein the matters in suspension vary widely in amount and character, the following table has been prepared, which contains representative data for a large number of determinations.

TABLE 1.

REPRESENTATIVE DUPLICATE DETERMINATIONS OF SUSPENDED MATTER BY THE GOOCH CRUCIBLE.

NATURE OF SAMPLE	SUSPENDED MATTER, PARTS PER MILLION			
	Total		Volatile	
Crude sewage	183	184	106	109
" "	310	314	148	152
" "	130	134	95	96
Settled sewage	125	128	92	94
" "	214	217	103	105
" "	266	267	130	128
Effluents of coarse-grain filters	144	139	45	44
" " " " "	63	67	24	21
" " " " "	88	89	26	24
Average	169	171	85	87

ACCURACY AND RELATIVE ADVANTAGES OF THE GOOCH CRUCIBLE AND THE PLATINUM EVAPORATION METHODS.

Total suspended matter.—It is evident that the data obtained from the Gooch method will more correctly represent the actual weight of suspended matter, inasmuch as in all other methods the efficiency of sedimentation and of the filtration is not sufficient to include colloidal matter or substances in a very fine state of subdivision. It would therefore be expected that slightly higher results would be obtained by the Gooch method, were all the other factors associated with the indirect platinum method left out of consideration.

To illustrate the extent to which the colloidal character of the suspended matter affects the accuracy of the usual indirect platinum method, the data in the following table are given. In this table widely different samples of crude sewage were examined by the platinum method in two ways; first, after the usual filtration through paper, and second, after filtration through asbestos, as in the Gooch

process. For the sake of comparison, the Gooch results were also included in the study.

The results show with considerable clearness the extent to which the efficiency of the filtration influences the results by the platinum method. The range of colloidal matter, as indicated from the data in the table below, is from 4 to 22, averaging 12 parts per million. From a practical standpoint it should be borne in mind that the platinum results are of equal value, since the suspended matter which is not included by the evaporation method forms a portion of that amount which cannot be removed by plain subsidence in an economical period of time.

TABLE 2.

REPRESENTATIVE RESULTS BY PLATINUM AND GOOCH METHODS, SHOWING THE EFFECT OF COLLOIDAL MATTER IN CRUDE SEWAGE.

SAMPLE OF CRUDE SEWAGE	SUSPENDED MATTER, PARTS PER MILLION			APPARENT COLLOIDAL MATTER, PARTS PER MILLION
	By Platinum Method Filtered through		By Gooch Method	
	Paper	Asbestos		
1	96	102	99	Max. 22
2	94	98	95	Min. 4
3	98	114	100	Average 12
4	72	86	96	
5	188	200	193	
6	170	192	180	
7	362	364	368	
8	196	210	223	

In the course of our investigations, a large number of determinations were made, comparing the Gooch and the platinum methods. The direct determination has always given higher results, ranging from 1 to about 33 per cent, and averaging about 13 per cent. As noted above, the completeness of the filtration seems to be one of the principal causes of these differences. The discrepancies are greatest where the suspended matters are low, and especially where they are more or less colloidal in character. Thus, in the table below it may be noted that the settled sprinkling filter effluents give the greatest variation, for in these the suspended matter is usually quite finely divided.

Without detracting from the value of the platinum results, which of course may be made more perfect by filtration through asbestos

or a Berkefeld filter,[1] our experience indicates that the Gooch crucible method is of more practical applicability, owing to the relatively greater facility and speed with which suspended matter data may be obtained. Relative results by the two methods are shown in the following table:

TABLE 3.

REPRESENTATIVE RELATIVE TOTAL SUSPENDED MATTER RESULTS BY GOOCH AND PLATINUM METHODS.

SOURCE OF SAMPLE	SUSPENDED MATTER, PARTS PER MILLION		PER CENT WHICH GOOCH RESULTS ARE HIGHER THAN PLATINUM RESULTS
	Gooch	Platinum	
Crude sewage	241	234	3
	636	632	1
	404	386	5
Settled sewage	186	164	12
	223	208	7
	103	78	24
Septic sewage	112	96	14
	146	122	16
	86	60	30
Coarse-grain filter	142	136	4
	211	196	7
	193	178	8
Settled effluents of coarse-grain filter	67	46	31
	89	70	21
	33	22	33
Average	.....	.....	13

THE INDIRECT DETERMINATION OF THE VOLATILE SUSPENDED MATTER.

It has been the practice for many years to ignite the dried and weighed residue upon evaporation of filtered and unfiltered samples, the loss in weight being taken to indicate the amount of organic matter present. The indirect determination of the volatile suspended matter is subject to a number of errors, as is well understood. In order that the residue shall be as free as possible from water of crystallization in the presence of incrustants, and to prevent to a considerable degree the loss of carbonic acid from magnesium salts also, and to convert all alkaline earth chlorides to the less volatile carbonates, it is customary to add a slight excess of sodium carbonate. Under such conditions, the residues do not usually contain water of crystallization, which will not be again taken up when the residues are moistened with water and evaporated. Owing to the complex and uncertain composition of the basic magnesium carbonate formed during the evaporation with sodium carbonate, considerable error is

[1] "Report of Committee on Standard Methods," *Jour. Infect. Dis.*, 1905, Supplm. No. 1, p. 44.

introduced upon ignition when magnesium is present, due to the loss of carbonic acid and some combined water.[1]

From the careful studies upon the "loss on ignition" made at Lawrence in 1890, it appears that the loss is approximately equal to 83 per cent of the weight of the magnesium (Mg) present. To determine further data upon this point, solutions of magnesium sulphate, in amount corresponding to 30, 60, 90, and 120 parts per million magnesium (Mg), were respectively treated with sodium carbonate in slight excess, evaporated in platinum, dried, and weighed. The dishes were then ignited for two minutes in the radiator, cooled, moistened with water, re-evaporated, dried, and weighed. Magnesium sulphate was used in this study for convenience. Since the magnesium of the alkalinity is also precipitated as a basic carbonate by heat and sodium carbonate, the end result of soda ash treatment is practically the same, whether or not, under natural conditions, incrustant magnesium is the only form in which the magnesium is present in the sewage.

From the results which appear in the table below, it is shown that the loss in weight, due to the loss of carbonic acid and combined water from the dried basic magnesium carbonate, is about 50 per cent of the total magnesium (Mg) present. As the average amount of magnesium (Mg) in the Columbus sewage is about 60 parts per million, the ignition of the residue of 50 c.c. of sewage entails a loss of 0.0015 gram, or 30 parts per million. These errors tend to balance each other in the unfiltered and filtered samples, so that the suspended loss is not affected to as marked a degree as might at first appear. The volatile matters, on the other hand, are obviously somewhat distorted.

TABLE 4.

LOSS IN WEIGHT UPON IGNITION OF MAGNESIUM SULPHATE AND SODIUM CARBONATE IN RADIATOR.
(Average of Two Experiments.)

Mg, Parts Per Million	Actual Weight Mg (Gram)	Actual Weight of Magnesium Sulphate and Sodium Carbonate	Loss in Weight after Two Min. Igni. (Gram)	Per Cent Loss in Weight
30	0.015	0.0146	0.0009	60
60	0.030	0.0285	0.0013	43
90	0.045	0.0413	0.0021	47
120	0.060	0.0556	0.0027	45
Average .	.....	.....	.....	49

THE DIRECT DETERMINATION OF VOLATILE SUSPENDED MATTER BY THE GOOCH CRUCIBLE METHOD.

The evidence seems to be very clear that the Gooch crucible method furnishes data upon volatile suspended matter which more

[1] *Mass. State Board of Health Report*, 1890, 2, p. 715.

correctly represent the actual conditions, since in this method the actual loss in weight resulting from the burning of the organic constituents is measured by a primary process.

When experiments were first begun looking to the feasibility of the adoption of the Gooch crucible, attention was soon directed to the great discrepancies existing between the volatile matter results obtained by the Gooch, as compared with those given by the platinum method. The extent of the variability of volatile suspended matter results by the two methods may be noted from the results in the following table:

TABLE 5.

COMPARATIVE VOLATILE SUSPENDED MATTER RESULTS BY GOOCH AND PLATINUM METHODS.

SOURCE OF SAMPLE	VOLATILE SUSPENDED MATTER		
	Parts per Million		Per Cent Which Platinum Is of Gooch
	Gooch	Platinum	
Crude sewage	132	96	72
	205	28	63
	174	148	85
Settled sewage	107	70	65
	124	96	77
	65	32	49
Septic sewage	74	56	76
	70	40	51
	74	46	62
Effluent of coarse-grain filter	45	28	62
	50	30	60
	48	24	50
Settled effluent of coarse-grain filter	23	2	17
	25	4	16
	23	4	17
Average	83	49	59

FACTORS ASSOCIATED WITH THE VARIABLE RESULTS OF THE INDIRECT EVAPORATION METHOD AS EXPLANATORY OF THE DISCREPANCIES EXISTING BETWEEN THE GOOCH AND PLATINUM METHODS.

The results given in the preceding table, showing such wide variation in the volatile suspended matter figures for the same example, but examined by two different methods, suggest that one of them must be open to serious criticism. Since in the Gooch method we are dealing with the actual suspended matter, it would appear that the discrepancies must be looked for in the indirect method, which, as is well understood, is subject to many inherent sources of error when it becomes a question of the absolute significance of the results.[1]

[1] *Mass. State Board of Health Report*, 1890, 2, p. 715.

One of the chief variables in the standard platinum method, which affects the indirect volatile suspended matter determination, refers to the incompleteness and uncertain character of the ignition. These irregularities have to do with the temperature of ignition, the time of ignition, and the relative amount and character of the mineral salts present. It is clear that the temperature of ignition must not be raised above the volatilization point of chlorides, nor above that at which oxygenated compounds become deoxygenated; and, as is well known, it is to avoid such complications that the radiator is used. Under such limitations it is apparent that the completeness of the combustion of the carbon will, in a large measure, depend upon its state of division, and perhaps upon the more important factor associated with the occluding property of the inorganic salts present. A close examination of residues ignited in platinum, according to the standard procedure, will show small particles of carbon remaining unoxidized. Since a complete ignition is understood to yield a residue white in color, save for the possible stain of oxide of iron, it is obvious that the present practice in regard to loss on ignition falls short of complete oxidation. Owing to the occlusion by the predominating mineral salts in residues from hard sewages, the loss on ignition results tend to be low, as already noted. To illustrate the

TABLE 6.

RELATIVE EFFECT OF SECOND IGNITION UPON THE TOTAL AND DISSOLVED VOLATILE MATTER.

CHARACTER OF SAMPLE	VOLATILE MATTER					
	Parts per Million				Per Cent Which First Ignition Is of Second Ignition	
	Total		Dissolved			
	1st Ignition	2d Ignition	1st Ignition	2d Ignition	Total	Dissolved
Crude sewage	72	92	44	54	78	81
	104	126	76	88	82	86
	98	106	78	82	91	95
Settled sewage	70	96	42	58	73	77
	178	200	114	122	89	93
	160	186	114	134	86	85
Septic sewage	74	110	40	58	67	70
	162	188	114	126	86	90
	182	208	126	156	88	81
Effluent of coarse-grain filter	68	98	40	52	70	77
	70	100	40	48	70	83
	66	108	40	50	61	80
Average	.....	.....	.....	.....	78	83

extent to which the occlusion of volatile matter by the mineral constituents of the residue is a factor in controlling the loss in weight on ignition, and also to illustrate what is thought to be one of the greatest sources of error in the determination of volatile suspended matter by the platinum method, the preceding table has been prepared, in which are presented data representative of a large number of determinations upon the point under discussion.

In the *Fourth Report of the Royal Bureau of Sewage Disposal and Water Purification* at Berlin,[1] in an account of the investigations at Cologne, Germany, the method used for the determination of the total and volatile suspended matter is given in detail. As refers to volatile matter, their method of ignition merits special comment, since it aims to ensure a very complete ignition, eliminating the occlusion factor to which we have already referred. In brief, the technique involves repeated ignitions, followed by applications of distilled water, until the small particles of carbon occluded by the mineral matter have entirely disappeared, leaving a pure white residue. Usually from four to six ignitions were necessary. To effect the ignition, the dish was moved cautiously back and forth over a free flame from a mushroom burner. As soon as considerable charring was noted, the residue was moistened with water, the water evaporated, and the ignition repeated as before. After the final ignition the residue was moistened with a few drops of ammonium carbonate solution, and then slightly warmed, in order to take up again the carbonic acid which might have been driven off in spite of the cautious heating.

Although, in the presence of magnesium, considerable error seems inevitable, yet this method appears to be an improvement over the ignition practices in this country, in which the occlusion of particles of organic matter by the mineral constituents of the residue is often a factor of considerable moment. To learn the extent to which the increased loss in weight could be attributed to the loss of carbonic acid from basic magnesium carbonate in the presence of sodium carbonate, a second ignition was made of the residues obtained in the magnesium experiments already described. It appears from these results that there may be an additional loss of about 8 per cent, or about five parts per million for 60 parts of magnesium (Mg), which is not to be traced

[1] *Report of Royal Bureau of Sewage Disposal and Water Purification*, Berlin, Germany, 1904.

to the more perfect combustion of the organic matter. Such errors as this obviously affect the total loss on ignition values rather than the volatile suspended matter results, as before mentioned. The effect of a second ignition upon basic magnesium carbonate is shown in the following table:

TABLE 7.

EFFECT OF SECOND IGNITION UPON BASIC MAGNESIUM CARBONATE.

(Mg) Parts per Million	Actual Weight Mg (Gram)	Loss in Total Weight (Gram)		Per Cent Total Loss in Weight	
		First Ignition	Second Ignition	First Ignition	Second Ignition
30.....	0.0150	0.0009	0.0010	60	67
60.....	0.0300	0.0014	0.0018	47	60
90.....	0.0450	0.0019	0.0023	43	51
120.....	0.0600	0.0023	0.0027	38	43
Average.....	.....	.....	.....	47	55

To determine the effect of further treatment with water and a second ignition in the radiator, residues from the usual processes have been so treated. Upon the reapplication of distilled water, and as a result of the second ignition, we have obtained residues containing no visible particles of carbon. How far the elimination of the occlusion factor will increase the value of the suspended loss on ignition results, the following comparative data may serve to illustrate. These results also indicate, in a general way, that a second application of water and a reignition of the residue from the first ignition would greatly enhance the value of loss on ignition data, bearing in mind the magnesium factor already discussed.

TABLE 8.

RELATIVE RESULTS BY GOOCH AND PLATINUM METHODS SHOWING EFFECT OF SECOND IGNITION.

Character of Sample	Volatile Suspended Matter, Parts per Million		
	Platinum Method		Gooch Method
	Two Minute Ignition	Second Ignition Three Minutes	
Crude sewage.....	28	38	43
" "	82	92	101
Settled sewage.....	28	38	44
" "	34	52	53
Effluent coarse-grain filter.....	30	52	50
	28	46	44
Settled effluent of coarse-grain filter.....	4	28	28
	4	30	30

SUMMARY AND CONCLUSIONS.

The results of these studies seem to show, with considerable clearness, the practical applicability of the Gooch crucible to the determination of the amount and character of the suspended matter in sewages and in sewage effluents. The advantages of the Gooch crucible method consist in accuracy, speed, and completeness of filtration, and the comparatively small number of operations entailed in its technique. Compared with the usual platinum evaporation method, and aside from the admitted superiority of a direct process, the use of the Gooch crucible very materially reduces the time and labor involved in manipulation. It eliminates the errors of the evaporation method, relating to uncertain amounts of water of crystallization in the dried total and dissolved residues, respectively, and the liability to a variable loss during ignition, due to deoxygenating decomposition and volatilization of certain mineral salts. As indicated also, the Gooch method not only gives results the equal of those obtained by the platinum method, but, when desired, it affords a practical means for estimating the amount of very finely divided suspended matter usually contained in sewages.

In the case of the platinum evaporation method, our results suggest the strong advisability that a second ignition should be included in the standard procedure, both for sewage and for polluted water, since by this means a more nearly perfect combustion of the organic matter seems assured at radiator temperature. An initial partial ignition of the residue, followed by the application of a small amount of distilled water, evaporation, and a second ignition, it is thought, would ensure a very complete oxidation of the organic matters at a low radiator temperature, thus obtaining the most efficient result at a temperature far below the volatilization point of mineral matter. Further, it is considered that asbestos could be used to advantage as a filtering material in sewage work, in order to effect a more complete removal of finely divided suspended matter than is possible by the use of filter paper.

During the investigations at Columbus, over 500 determinations of suspended matter were made by the Gooch crucible method, in samples ranging from the crude sewage containing as high as 1,500 parts per million of total suspended matter, to settled effluents from

sprinkling filters containing as low as 20 parts per million of suspended matter, duplicate results showing that the method was at least applicable to this range of suspended matter in amount and character.

Such being the range of the applicability of the Gooch crucible method and in view of the several advantages it possesses over the indirect platinum method for the determination of suspended matters, the conclusion seems justified that, for practical routine work upon sewage, especially in investigations relating to physical questions involved in sewage purification, the Gooch crucible method deserves recognition as a standard method.

In conclusion the writers desire to express their thanks to Mr. Julian Griggs, chief engineer of the Board of Public Service, Columbus, Ohio, through whose courtesy they have been permitted to publish the results of these studies in advance of the regular testing-station report. Further, they desire heartily to acknowledge the valuable criticisms of Mr. George W. Fuller, consulting engineer, and the helpful suggestions of Mr. George A. Johnson, engineer in charge of the Columbus Testing Station.